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ON MEASUREMENTS OF FORMATION, GROWTH,  
HYGROSCOPICITY, AND VOLATILITY OF  
ATMOSPHERIC ULTRAFINE PARTICLES

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Academic dissertation

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# **On measurements of formation, growth, hygroscopicity, and volatility of atmospheric ultrafine particles**

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University of Helsinki, 2006

## **Abstract**

Atmospheric aerosol particles affect the global climate as well as human health. In this thesis, formation of nanometer sized atmospheric aerosol particles and their subsequent growth was observed to occur all around the world. Typical formation rate of 3 nm particles at varied from 0.01 to 10 cm<sup>-3</sup>s<sup>-1</sup>. One order of magnitude higher formation rates were detected in urban environment. Highest formation rates up to 10<sup>5</sup> cm<sup>-3</sup>s<sup>-1</sup> were detected in coastal areas and in industrial pollution plumes. Subsequent growth rates varied from 0.01 to 20 nm h<sup>-1</sup>. Smallest growth rates were observed in polar areas and the largest in the polluted urban environment. This was probably due to competition between growth by condensation and loss by coagulation.

Observed growth rates were used in the calculation of a proxy condensable vapour concentration and its source rate in vastly different environments from pristine Antarctica to polluted India. Estimated concentrations varied only 2 orders of magnitude, but the source rates for the vapours varied up to 4 orders of magnitude. Highest source rates were in New Delhi and lowest were in the Antarctica.

Indirect methods were applied to study the growth of freshly formed particles in the atmosphere. Also a newly developed Water Condensation Particle Counter, TSI 3785, was found to be a potential candidate to detect water solubility and thus indirectly composition of atmospheric ultra-fine particles. Based on indirect methods, the relative roles of sulphuric acid, non-volatile material and coagulation were investigated in rural Melpitz, Germany. Condensation of non-volatile material explained 20-40% and sulphuric acid the most of the remaining growth up to a point, when nucleation mode reached 10 to 20 nm in diameter. Coagulation contributed typically less than 5%. Furthermore, hygroscopicity measurements were applied to detect the contribution of water soluble and insoluble components in Athens. During more polluted days, the water soluble components contributed more to the growth. During less anthropogenic influence, non-soluble compounds explained a larger fraction of the growth. In addition, long range transport to a measurement station in Finland in a relatively polluted air mass was found to affect the hygroscopicity of the particles. This aging could have implications to cloud formation far away from the pollution sources.

Keywords: Atmospheric aerosols, aerosol measurements, particle formation and growth, hygroscopicity, volatility

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## List of publications

This thesis consists of an introductory review, followed by six research articles. In the introductory part, these papers are cited according to their roman numerals.

- I** Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W. and McMurry, P.H. (2004) Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.*, 35, 143–176.
- II** Kulmala, M., Petäjä, T., Mönkkönen, P., Koponen, I.K., Dal Maso, M., Aalto, P.P., Lehtinen, K.E.J. and Kerminen, V.-M. (2005) On the growth of nucleation mode particles: source rates of condensable vapour in polluted and clean environments. *Atmos. Chem. Phys.*, 5, pp. 409–416, SRef-ID: 1680-7324/acp/2005-5-409.
- III** Petäjä, T., Kerminen, V.-M., Dal Maso, M., Junninen, H., Koponen, I.K., Hussein, T., Aalto, P.P., Andronopoulos, S., Robin, D., Hämeri, K., Bartzis, J.G. and Kulmala, M. (2006) Sub-micron atmospheric aerosols in the surroundings of Marseille and Athens: Physical characterization and new particle formation. *Atmos. Chem. Phys. Discuss.*, 6, pp. 8605–8647.
- IV** Wehner, B., Petäjä, T., Boy, M., Engler, C., Birmili, W., Tuch, T., Wiedensohler, A. and Kulmala, M. (2005) The contribution of sulfuric acid and non-volatile organics on the growth of freshly formed atmospheric aerosols. *Geophys. Res. Lett.*, 32, L17810, doi:10.1029/2005GL023827.
- V** Petäjä, T., Kerminen, V.-M., Hämeri, K., Vaattovaara, P., Joutsensaari, J., Junkermann, W., Laaksonen, A. and Kulmala, M. (2005) Effects of SO<sub>2</sub> oxidation on ambient aerosol growth in water and ethanol vapours *Atmos. Chem. Phys.*, 5, 767–779, Sref-ID: 1680-7324/acp/2005-5-767.
- VI** Petäjä, T., Mordas, G., Manninen, H., Aalto, P.P., Hämeri, K. and Kulmala, M. (2006) Detection efficiency of a water-based TSI Condensation Particle Counter 3785. *Aerosol Sci. Technol.* (in press).

**Paper I** is reprinted from J. Aerosol Sci., 35, Kulmala, Vehkamäki, Petäjä, Dal Maso, Lauri, Kerminen, Birmili and McMurry, Formation and growth rates of ultrafine atmospheric particles: a review of observations, copyright (2004), with permission from Elsevier. **Papers II, III and V** are reprinted under Creative Commons Licence. **Paper IV** is reproduced by permission of American Geophysical Union. **Paper VI**, Detection efficiency of a water based TSI condensation particle counter 3785 by Petäjä, Mordas, Manninen, Aalto, Hämeri and Kulmala, copyright (2006), is reproduced by permission from Taylor & Francis, Inc., <http://www.routledge-ny.com>.

# 1 Introduction

Aerosol is by definition a mixture of solid or liquid aerosol particles suspended in a gaseous medium (Hinds, 1999). In the Earth’s atmosphere aerosol particles are ubiquitous. Their size ranges from nanometers to several tens of micrometers in diameter. This thesis concentrates on atmospheric ultra-fine particles (less than 100 nm in diameter), which is in number, the dominating fraction in the ambient conditions.

Atmospheric aerosol particles affect the global climate directly by scattering incoming solar radiation and indirectly by acting as a cloud condensation nuclei (CCN). Regionally, suspended particulate matter deteriorate visibility (Cabada et al., 2004) and has negative effects on human health (Brunekreef and Holgate, 2002; Von Klot et al., 2005). The net effects depend on the amount of particles, their chemical composition, and their physical size.

Ultra-fine particle population is renewed by both primary (Kittelson et al., 2004) and by secondary sources i.e. gas-to-particle conversion (**Paper I**). Both anthropogenic sources (Kittelson et al., 2004; Janhäll and Hallquist, 2005) and biogenic sources (Tunved et al., 2006) contribute to the amount of suspended ultra-fine aerosol particle number concentration.

In the assessment of the indirect climatic effects of ambient aerosol particles, global models (Stier et al., 2005; Spracklen et al., 2006) has to be utilized. Regional air quality models (Sotiropoulou et al., 2004) can be put to use to calculate e.g. particulate pollution exposure of the population in the modeling domain. Both of these applications need measured properties of ambient aerosol particle population and hygroscopicity as input parameters (Putaud et al., 2004). Thus, both modeling and measurements are needed to evaluate and refine global and regional aerosol effects.

The main objective of this thesis is to gain insight into the formation of new atmospheric aerosol particles and the processes contributing to their subsequent growth. In addition, this thesis had several individual aims:

- to summarize observed new particle formation events and subsequent growth episodes worldwide,
- to estimate the concentration and source strength of a model condensable vapour compound, which would explain the observed growth rate in various environments,



- to examine the role of sulphuric acid, non-volatile material and coagulation on the growth rate of newly formed particles during selected case studies,
- to develop further experimental methods to quantifying different mechanisms responsible for the observed growth of nucleation mode particles in the atmosphere,
- to present differences and similarities of air-mass origin to hygroscopic properties (and tentatively chemical composition) of nucleation and Aitken mode particles in Hyytiälä, Finland, and
- to quantify the effect of variable chemical composition on the detection efficiency of a commercially available Condensation Particle Counter.

## 2 Experimental methods

The experimental methods presented in this thesis concentrate on the detection of particles below  $0.1\mu\text{m}$  in diameter. Furthermore, they rely on on-line methods, where the ambient particle concentration, size distribution, hygroscopicity and volatility is determined typically in less than 10 minute time resolution. With presented methods, no material is collected for later analysis in a laboratory.

The detection and measurements of atmospheric ultra-fine aerosol particles consist of several steps in sequence (Brockmann, 2001; Aalto, 2004). First, the particles need to be transported from the ambient air to the sampling system using an inlet, which removes unwanted particles letting the desired particles to enter the measurement setup with highest possible efficiency regardless of e.g. wind velocity. In this work, low flow PM10 (Thermo Anderson, USA) inlet was used in **Paper IV**. In **Papers III,V**, and partly in **II**, a Stainless Steel tube with a simple rain cover was used as the inlet.

The next step in the measurement process is conditioning of the ambient aerosol population to a desired relative humidity (RH), temperature or electrical charging state. Typically number size distribution measurements of sub-micron particles are conducted at relative humidity (RH) less than 30%. Otherwise their hygroscopic growth would distort further steps of the measurement process. The aerosol sample was dried with a Perma-pure drier in **Paper III** and during some of the campaigns in **Paper II**. In **Paper V** the sample was not dried, since the during winter-time ambient absolute humidity is low and as the sample was brought to room temperature, the relative humidity

remained low. In **Paper IV**, the ambient sample was conditioned to a temperature of 300°C to evaporate any volatile components from the aerosol phase.

The size classification used in this thesis relies on the mobility of charged particles in an electric field. Vienna-type Differential Mobility Analyzers (DMA, Winklmayr et al. (1991)) were used to segregate the sampled population according to their electrical mobility, which is, in turn, a function of their physical size. Electrical charging was done using radioactive sources. This generates a vast number of ions which attach to the sampled particles. This enables size classification of the sampled particles based on their electrical mobility in a constant electric field.

At all stages of the measurement procedure, ultra-fine particles are lost due to their high diffusivity. Thus, the whole measurement setup has to be constructed so that the sampling lines remain as short as possible.

## 2.1 Condensation Particle Counter (CPC)

In this study, concentration of atmospheric particles were measured with the aid of Condensation Particle (Nucleus) Counters (CPC, CNC). In a CPC the initial size of the sampled aerosol particles are increased by condensing a supersaturated vapour onto the surface of the particles. The particles become large enough to be detected with optical methods. This is a very powerful method to measure concentration of particles that contain only a small amount of mass and are therefore difficult to detect by any other means (McMurry, 2000).

The properties of the condensing vapour (and particles) and the degree of the supersaturation determine the smallest size of a particle, which can be activated inside the CPCs (Mertes et al., 1995; Sem, 2002). The most frequently used substances as the condensing vapour are water and alcohols. Several methods for producing the supersaturation have been suggested including conductive cooling (Bricard et al., 1976), turbulent mixing of cool and warm saturated air (Kousaka et al., 1982), and adiabatic expansion (Aitken, 1897; Kürten et al., 2005). Most widely used are conductive cooling type CPCs since they can be operated together with analyzers operating in a continuous flow. In a conductive cooling CPC, the sampled particles are first saturated with a vapour at a higher temperature and then brought into a cooled condenser, where the supersaturated vapour condenses onto the particles. Subsequently the droplets are

counted with optical methods.

The most important parameter for the condensation particle counters is its detection efficiency as a function of the particle size. A more practical parameter is a cut-off size,  $D_{50}$ . It is a diameter at which the 50% of the sampled particles are successfully counted with the instrument. The cut-off size depends on the aerosol losses in the inlet of the CPC, the efficiency of the optical system, and the particle activation efficiency. However, Stolzenburg and McMurry (1991) showed that the cut-size is mostly a function of the activation efficiency alone. In other words, the detection efficiency is determined by the amount of supersaturation generated inside the instrument. Mertes et al. (1995) showed that in a conductive cooling CPC operating on butanol condensation, the detection efficiency can be tuned by applying a different temperature difference between the saturator and the condenser of the instrument.

A recently developed TSI 3785 continuous flow water-based CPC (WCPC, Hering et al. (2005)) was characterized in the laboratory conditions as a part of this thesis (**Paper VI**). A schematic picture of the WCPC is presented in Figure 1. In nominal operation conditions, the supersaturation inside the WCPC is generated by saturating the sample with water at room temperature and then directing the sample to a heated growth tube ( $60^{\circ}\text{C}$ ), where the particles are activated and later on counted. The temperature difference is reversed in comparison with the traditional conductive cooling CPCs. With water vapour, the supersaturation at high temperatures are realised by the fact that the mass diffusivity of the vapour is higher than thermal diffusivity of air (Hering and Stolzenburg, 2005). In other words, in the growth tube, water vapour is transported more efficiently than the temperature is equalized at the centerline of the growth tube. Despite the reversed temperature settings, in **Paper VI** it was found that the detection efficiency of the WCPC can be tuned by changing the temperature difference between the conditioner and the growth tube.  $D_{50}$  values for silver particles varied between 4 and 14.5 nm as a function of the temperature difference (**Paper VI**). This enables the user to select a desired cut-off size depending on the need.

In **Paper VI** the effect of particle composition to the detection efficiency was investigated. The results in the **Paper VI** corroborated the earlier study by Hering et al. (2005) that the composition has an effect on how well the WCPC detects particles.  $D_{50}$  values for water soluble sodium chloride and ammonium sulphate were 3.6–3.8 and 5.1 nm, respectively, at nominal operation conditions. For insoluble silver it was 5.8 nm (**Paper VI**). This difference increased as lower temperature differences were applied.

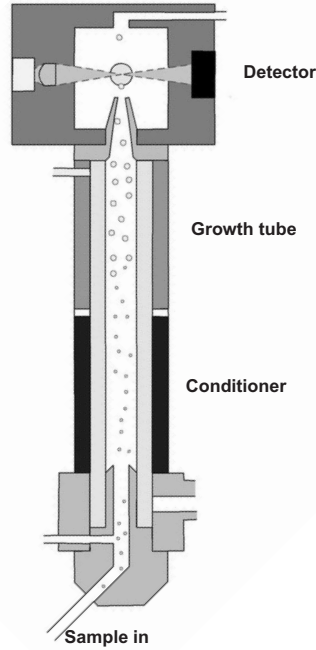


Figure 1: A schematic picture of a TSI 3785 Condensation Particle Counter (modified from Hering et al. (2005)).

At ambient concentrations, the WCPC was compared against more widely used butanol based CPC (TSI model 3022A) by Biswas et al. (2005). They found a good correlation between the instruments and an agreement up to particle concentration of  $40\,000\text{ cm}^{-3}$ . But a variable cut-off as a function of particle composition (**Paper VI**) is a major drawback considering measurements of ambient ultra-fine particles, where the constituents in the particulate phase varies both temporally and spatially. In particular this has an effect on the measured concentrations, when a lot of nucleation mode particles are present. However, this effect can be utilized to extract information on the composition of ambient particles, when a WCPC is applied in parallel with a butanol based CPCs (Kulmala et al., 2006b).

## 2.2 Differential Mobility Analyzer (DMPS)

Ambient sub-micron aerosol particle size distribution measurements were performed with a Differential Mobility Particle Sizer (DMPS) in **Papers II, III, IV and V**. A schematic picture of the instrument is presented in Figure 2. In fact, the DMPS system (Aalto, 2004) consists of two parallel DMPS systems (twin-DMPS) with a closed loop flow arrangement (Jokinen and Mäkelä, 1997). The first set is dedicated to smaller particles, typically from 3 nm up to 50 nm in diameter. These particles are counted with a TSI-CPC 3025 ultra-fine particle counter (Stolzenburg and McMurry, 1991). The second DMPS measures particles up to 1000 nm in diameter. They are detected with a TSI CPC 3010 (Mertes et al., 1995). Size classification is done using Vienna type Differential Mobility Analyzers (DMA, Winklmayr et al. (1991)).

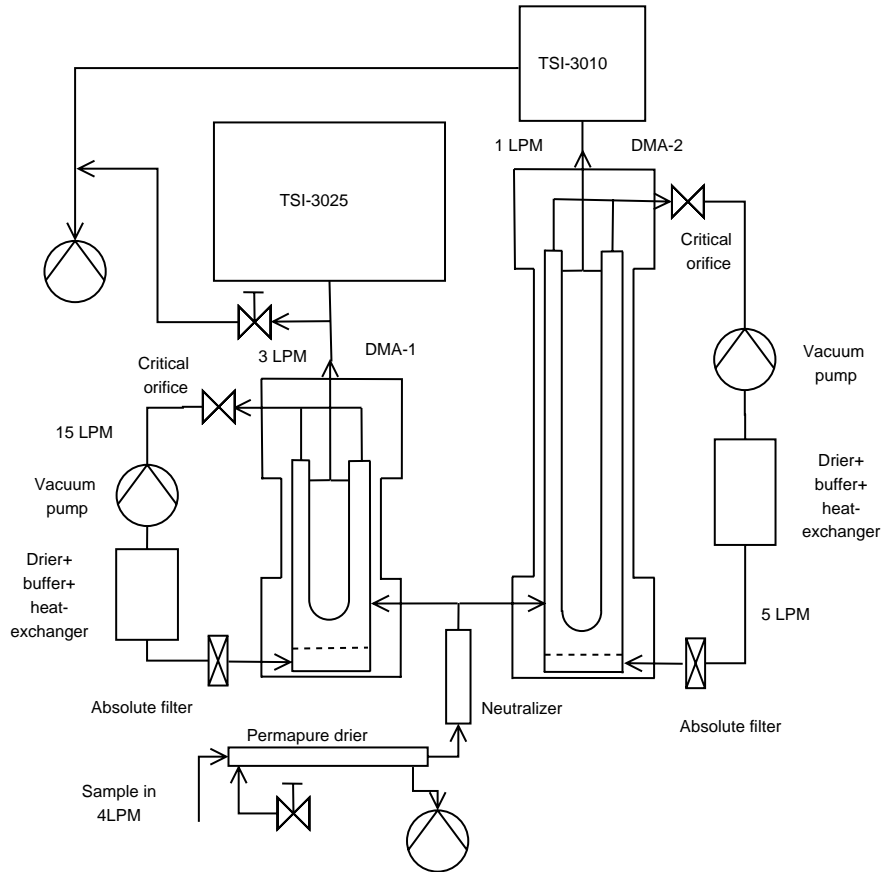


Figure 2: A closed loop twin Differential Mobility Particle Sizer (DMPS, Aalto (2004))

Time resolution of the DMPS is 10 minutes. The total sub-micron aerosol number

concentration is obtained from the integrated size distributions. A more detailed description of the instrument can be found in Koponen (2003) and Aalto (2004).

### 2.3 Thermodenuder (TD)

In **Paper IV** volatility of the ambient aerosol particles was studied using a Thermodenuder (Philippin, 2000; Wehner et al., 2002). Its schematic illustration is presented in Figure 3. The TD consists of two sections, one heated and one cooled. In the heated section, volatile material evaporates from the aerosol phase to the gaseous phase. Inside the cooling section, the aerosol-vapour mixture temperature decreases close to room temperature. To hinder re-condensation, the cooling tube is surrounded by an active carbon reservoir which absorbs the vapours.

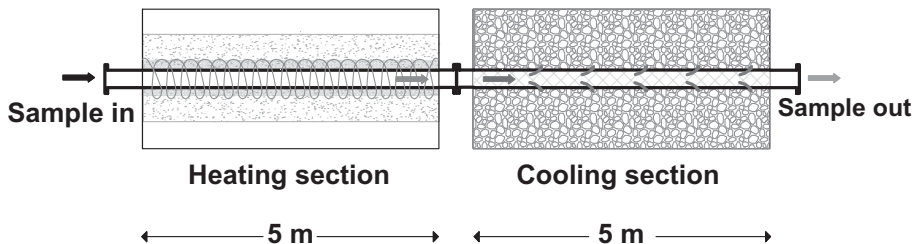


Figure 3: Thermodenuder (TD), modified from Wehner et al. (2002).

The thermodenuder was placed before a DMPS setup which sampled automatically alternating between a TD set at 300°C and a dummy, unheated TD in **Paper IV**. At 300°C sulphate, nitrate, ammonium, and part of organic carbon evaporated from the aerosol phase. The remaining compounds are non-volatile soot, trace metals, fly ash, crustal material, sea salt and carbonaceous compounds (Wehner et al., 2002). The same DMPS system was used for both volatility and normal measurement, which ensured comparability of the measurements after correction the TD side from thermophoretic losses inside the heated section.

### 2.4 Hygroscopic Tandem Differential Mobility Analyzer (HTDMA)

Chemical analysis of nucleation mode particles has proven to be extremely difficult owing to their minuscule mass. Recently the sensitivity of the analysis has improved,

and even speciation of single nucleation mode particles in the laboratory has been determined (Wang et al., 2006). In the atmospheric conditions, analysis is possible during a growth period of freshly formed particles in the sub-20 nm size range (Smith et al., 2005).

Species in the nucleation mode particles can be inferred indirectly from their hygroscopicity i.e. how much they absorb water vapour in sub-saturated conditions. In **Papers III** and **V** a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA, Rader and McMurry (1986); Hämeri et al. (2000)) was applied to study water vapour uptake of ultra-fine atmospheric aerosol particles. A schematic picture of the HTDMA is presented in Figure 4.

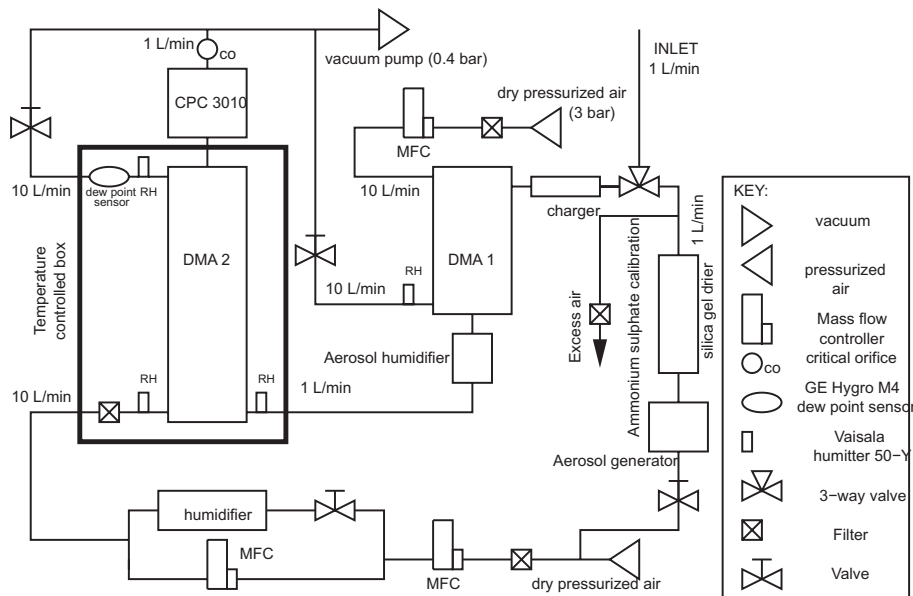


Figure 4: A Hygroscopic Tandem Differential Mobility Analyzer (HTDMA, Petäjä (2004))

The HTDMA setup consists of two Vienna (Winklmayr et al., 1991) DMAs in series. The first one is used to select a monodisperse sample from ambient particle population. Then the second DMA is scanned through a size spectrum corresponding to a range of 0.9–2.2 times the selected dry sample size. The concentration of particles is measured with a TSI 3010 CPC.

A controlled amount of water vapour is added to the sheath flow and the aerosol flow of a second DMA. The relative humidity (RH) in the sheath and excess flows are monitored with Vaisala HMM-211 dew point sensors ( $\pm 2\%$  at 0–100%). An additional

humidifier is placed in the aerosol flow from DMA1 to DMA2 to ensure high enough RH inside the DMA2 and to increase residence time of the particles at the elevated water vapour conditions. Aerosol humidifier is controlled to 82% RH and monitored with a Vaisala 50Y-sensor ( $\pm 3\%$  at 0-90%RH). A Hygro M4 dew point sensor with a chilled mirror sensor (D2) is used as an internal reference for the RH ( $\pm 1.25$  RH at 95%). A more detailed description of the HTDMA setup can be found in Zhou (2001) or Väkevä (2002).

As the initially dry particles absorb water, their size increases due to water condensation. The increment is a function of particle composition as well as relative humidity inside the system. Since the RH is constant, the changes in particle growth are related to differences in chemical composition of sampled particles. Typically inorganic salts, such as ammonium sulphate, absorb water vapour in large quantities (Hämeri et al., 2000). On the other hand, water vapour is condensed onto organic components to a lesser extent (Virkkula et al., 1999; Petäjä, 2004; Carrico et al., 2005) excluding some organic acid salts (Peng et al., 2001). The instrument can also detect, whether the components are externally or internally mixed within the particle population (Väkevä et al., 2002; Aklilu and Mozurkewich, 2004).

The output of the HTDMA setup is a growth factor (GF) spectrum of the initially monodisperse sample at elevated relative humidity. Measured GFs can be converted into a soluble fraction. The sampled particles are assumed to consist of two volumes, one completely inert to the surrounding water vapour and one behaving as ammonium sulphate (Swietlicki et al., 1999). The evolution of hygroscopic growth factors and derived soluble fractions at a constant relative humidity from HTDMA give an independent estimation on the relative contribution of water soluble and insoluble components to nucleation mode growth (Kulmala et al., 2001b). Moreover, when hygroscopicity is monitored in parallel with TDMA systems relying on other condensing vapours, e.g. ethanol (Joutsensaari et al., 2001) as in **Paper V**, mass fluxes of water soluble and insoluble as well as ethanol soluble and insoluble compounds can be estimated. Applying also concurrent volatility (Ehn et al., 2006b) and Condensation Particle Counter Battery (Kulmala et al., 2006b), these indirect methods could give quite a complete picture of the properties of the participating in the ultra-fine particle growth in the atmosphere.



## 3 Results and discussion

### 3.1 New particle formation in the atmosphere

Formation of new atmospheric particles is observed to occur all around the global atmosphere (**Paper I** and references therein). Subsequently new particle formation has been reported to occur e.g. in pristine areas in Lapland (Vehkamäki et al., 2004a; Komppula et al., 2006) and in Antarctica (Koponen et al., 2003), in the suburban and rural Mediterranean Area (Marinoni et al. (2005); Rodríguez et al. (2005), **Paper III**), continental Europe at ground level (Held et al., 2004) and based on balloon borne measurements (Stratmann et al., 2003; Siebert et al., 2004) and in a mountain ridge during cloud-outflow conditions (Mertes et al., 2005), in Fresno, U.S. (Watson et al., 2006), in relatively polluted region of Pittsburgh, U.S. (Stanier et al., 2004) and Atlanta, U.S. (Stolzenburg et al., 2005a), in extremely polluted New Delhi (Mönkkönen et al., 2005), Beijing (Wehner et al., 2004) and Mexico City (Dunn et al., 2004), in Sierra Nevada, USA (Lunden et al., 2006), in beech forest in Denmark (Pryor et al., 2005), over the Yellow Sea during a continental outflow (Buzorius et al., 2004), in West coast of the U.S. (Wen et al., 2006) and in the cloud outflow e.g. in the Indian Ocean (Kamra et al., 2003).

In the atmosphere, typical formation rate of 3 nm particles varied from 0.01 to 10  $\text{cm}^{-3}\text{s}^{-1}$ . In the polluted urban areas, the formation rate was up to one order of magnitude higher and in the industrial plumes and in coastal areas, formation rates up to  $10^5$  were reported (**Paper I**).

New particle formation in the atmosphere is initiated by nucleation, where a new phase is formed within a pre-existing phase (Kulmala, 2003). The exact mechanism and participating compounds responsible for the phase transition remains unknown. Several different theories have been proposed, e.g. binary nucleation of sulphuric acid and water (Mirabel and Katz, 1974; Kulmala, 1988), ternary nucleation of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  (Korhonen et al., 1999), biogenic iodine (O’Dowd et al., 2002), barrierless kinetic nucleation (Weber et al., 1996; Lushnikov and Kulmala, 2001), activation (Kulmala et al., 2006a), organic nucleation (Marti et al., 1997), and ion-induced nucleation (Yu and Turco, 2000).

Which of the proposed mechanisms dominate, depend on e.g. temperature, height,

meteorological conditions, air mass history, geographical location, amount of solar radiation and radioactivity and trace gases (ammonia, sulphuric acid, oxidation products of volatile organic compounds) and extent of condensation sink provided by pre-existing particle population.

Sulphuric acid is the one of the key elements contributing to the initial step of the formation of new atmospheric particles (Weber et al., 1996), but binary sulphuric acid-water system explains only some measurements in the free troposphere (Andronache et al., 1997). Ternary nucleation of sulphuric acid, water and ammonia predicted successfully the formation of new particles in polluted conditions (Stanier et al., 2004). Recently, formation through activation of molecular sulphuric acid clusters was applied to a global model (Spracklen et al., 2006). Modeled formation reproduced well the long term temporal new particle formation statistics in the Boreal Forest dominated boundary layer.

The role of various organic compounds in the atmospheric nucleation process itself has been studied actively, since the oxidation products of volatile organic compounds (VOC) of both biogenic and anthropogenic origin are able to produce new particles in laboratory conditions (Odum et al., 1997; Hoffmann et al., 1998). Unfortunately the concentrations used in the environmental chambers are typically orders of magnitude higher than observed ambient concentrations. However, interaction between sulphuric acid and organic acids seem to promote new particle formation (Zhang et al., 2004). Thus, the organic compounds cannot be neglected in the formation process under atmospheric conditions.

Thermodynamic barrier for the phase transition can be lower, when charged ions are present. This ion-mediated nucleation is, on the other hand, constrained by the ion production rate due to external radiation (radon) and galactic cosmic rays (Laakso et al., 2004). With two independent methods Laakso et al. (2004) determined ion production rate during spring 2003 in Hyytiälä, Finland. The average rate was 2.6 and 4.5 ion pairs  $\text{cm}^{-3}\text{s}^{-1}$  based on measured ion - aerosol particle concentrations and external radiation and radon concentrations, respectively. Based on the data from a modified version of a conventional Differential Mobility Analyzer, Laakso et al. (2006) reported that both neutral and ion-mediated nucleation events occurred in Hyytiälä, Finland during spring 2005. Typically less than 10% of the formed particles were accounted for by the ion induced nucleation. The contribution varied from day to day from zero to almost 100%. Further measurements and data analysis is needed

to extract seasonality of the relative contribution of ions and neutral clusters in the formation.

Kulmala et al. (2000) anticipated the presence of small neutral clusters in the boundary layer due to constant production of tiny,  $\sim 1$  nm thermodynamically stable clusters. According to Vehkamäki et al. (2004b), theoretically almost all the sulphuric acid in the atmosphere would be bound as stable clusters, such as ammonium-bisulphate, in the atmosphere. This would reduce the formation threshold, since the phase transition has already commenced. There is no direct experimental proof for these results. Tentatively Kulmala et al. (2005a) detected neutral clusters in the Boreal Forest atmosphere using modified Condensation Particle Counters as a nucleation chamber.

To summarize, a vast amount of different theories have emerged during the last decade or so, all of them applicable and able to explain observed new particle formation events to at least to some parts of the atmosphere, geographically or vertically. Most probably not a single mechanism will not be able to predict occurrences of new particles in the ambient conditions in all locations. Discrepancies between the observations and the theories have lead to both instrumental development and refined theories, which both are far from being completed.

### **3.2 Growth, hygroscopicity and volatility**

Online chemical characterization using e.g. Aerosol Mass Spectrometer (Jayne et al., 2000), Thermal Desorption Chemical Ionization Mass Spectrometer (Voisin et al., 2003) are special methods, which are only rarely available. The sensitivity of the instruments is improving. Smith et al. (2005) was able to determine composition of growing nucleation mode in atmosphere in urban environment and Wang et al. (2006) was able to speciate even single 10 nm particles in laboratory conditions. However, due to minuscule masses involved, direct methods are still not sensitive enough to characterize composition of freshly formed atmospheric particles in the conditions, where concentration of the ultra-fine particles is small. In these cases, one has to rely on indirect observation methods, which reflect the changes taking place in the composition of nucleation mode particles during their growth towards climatically active sizes.

In this thesis, two aerosol properties which can be used to tentatively identify participating compounds in the growth of atmospheric nucleation mode particles, namely

hygroscopicity (**Paper III**) and volatility (**Paper IV**) and their temporal variabilities, were examined. Furthermore, the verification of the water-based Condensation Particle Counter (WCPC, Hering et al. (2005)) detection efficiency in the laboratory conditions are presented in **Paper VI**. The detection efficiency was found to be dependent on the chemical composition of the sampled particles. Initially smaller water soluble inorganic compounds are perceived with a greater efficiency than more hydrophobic particles (**Paper VI**). Thus, using a WCPC in parallel with a butanol based counter initially set up to have a same cut-off diameter for an inert calibration aerosol yields information on the composition of particles below 10 nm in diameter (Kulmala et al., 2006b).

According to the review (**Paper I**), the observed growth of the freshly nucleated particles in the atmosphere varies between 0.1 and 20 nm h<sup>-1</sup>. Smallest growth rates were observed in polar areas and the largest in the polluted urban environments. This is probably due to competition between growth by condensation and loss by coagulation. The larger the pre-existing sink is, the faster the formed particles need grow so that the growth is detected and not all the formed particles are lost by collisions with background particles (**Paper II**).

The processes growing the newly formed particles in the atmosphere are condensation of *e.g.* sulphuric acid, and oxidation products of different volatile organic compounds, as well as intra- and extramodal coagulation (*e.g.* Stolzenburg et al. (2005a), **Paper IV**). Their relative roles are bound to vary from one geographical location to another due to differences in the gaseous precursor emission fingerprints and strengths as well as variability of the pre-existing particle population which acts as a sink for both freshly nucleated particles and the condensable vapours.

Sulphuric acid is the one of the key elements contributing to the initial steps of the formation of new atmospheric particles (Weber et al., 1996) as well as on their subsequent growth. Kulmala et al. (2001a) presented analytical methodology, how to estimate needed sulphuric acid concentrations and its production rates which would explain the observed growth. This was applied to a variety of environments in **Paper II**. There was only small variations in the observed growth rates in ambient conditions between polar areas and urban environment. The estimated source rates, however, varied more than 4 orders of magnitude from  $9 \cdot 10^2$  to  $1 \cdot 10^7$  cm<sup>-3</sup>s<sup>-1</sup> between Antarctica and New Delhi, respectively (**Paper II**).

There is, however, a discrepancy between the sulphuric acid concentrations and estimated condensable vapour concentrations based on observed growth rates (Kulmala et al., 2001a). Based on data from Hyytiälä, Finland, Kulmala et al. (2001a) concluded that the observed growth was not possible by the sulphuric acid alone. Thus, additional compounds are needed to participate in the growth process (Kulmala et al., 2001b). Oxidation products of monoterpenes are a plausible candidate (Kavouras et al., 1999; Janson et al., 2001; Sellegri et al., 2005). Also products of more reactive sesquiterpenes (Bonn and Moortgat, 2003) as well as even isoprene (Claeys et al., 2005) could have an effect on the growth.

More specific, (Boy et al., 2005) compared measured and modeled sulphuric acid concentrations and their contribution to the nucleation mode growth in Hyytiälä, Finland. According to Boy et al. (2005), on average only 10% of the observed growth could be attributed to sulphuric acid in the Boreal Forest. No significant effect of air mass origins from clean or continental Europe was observed. Similar results were extracted by Fiedler et al. (2005) when comparing sulphuric acid contribution to the nucleation mode growth in Hyytiälä in Finland and Heidelberg in Germany. In addition, contribution to the growth, according to their results, was up to 20% in the size range below the detection limit of the DMPS ( $D_p=1-3$  nm). Generally in this size range, the growth rate is lower than above ten nanometer particles (Hirsikko et al., 2005). On the other hand, Stolzenburg et al. (2005a) was able to explain almost 100% of the observed growth by sulphuric acid and coagulation processes in sulphur-rich Atlanta, USA, during four out of six case studies. In the remaining two days, observed growth rates were by a factor of three larger than calculated ones. This leaves a door open for other, possibly organic vapours, to contribute to the observed growth even in the environment where sulphuric acid concentrations are higher than in rural Finland.

The large contribution of sulphuric acid to the observed growth in Atlanta was supported by independent hygroscopicity and volatility measurements in size range below 10 nm by Sakurai et al. (2005). During the nucleation events, the particles had high hygroscopic growth factors at 90% RH, and were nonvolatile at 100°C. In addition, parallel online chemical speciation (Smith et al., 2005) showed enhanced concentration of ammonium sulphate in the size range below 15 nm in diameter during nucleation events. Whether or not this holds also for a more remote areas needs to be clarified with a combined measurement and modeling effort.

The relative roles of different mechanisms to particle growth in a rural site at Mel-

pitz, Germany was examined in **Paper IV**. Four new particle formation days were analyzed, and the observed growth was divided between condensation of sulphuric acid, accumulation of non-volatile core material and coagulation. Volatility analysis at 300°C (**Paper IV**) with a thermodenuder (Wehner et al., 2002) showed clearly that during the selected four days, nucleation mode did not evaporate completely during the growth period. At 300°C, sulphate, nitrate, ammonium and part of organic carbon evaporates from the aerosol phase. The remaining compounds are non-volatile soot, trace metals, fly ash, crustal material, sea salt and carbonaceous compounds (Wehner et al., 2002). Typically from those only soot and carbon containing compounds are found in the nucleation mode particles. The fact that a continuous accumulation of this non-volatile core material was detected (**Paper IV**) indicates that the non-volatile material is not soot, but organic carbon condensing onto the nucleation mode particles as they grow during daytime. One possible explanation is heterogeneous production of polymers within the particles, which is observed to take place in the environmental chambers, when organic precursors form new particles, grow and, with time, transform the material within the particles into non-volatile polymers (Kalberer et al., 2004).

To conclude on the results of (**Paper IV**), non-volatile core material condensation contributed 20-40%, and coagulation typically less than 5%. The rest was attributed to the calculated sulphuric acid obtained from a closure model (Boy et al., 2005). These processes explained almost all the observed growth until the nucleation mode had reached 10-20 nm in diameter. The agreement dissipated subsequently. This tentatively indicates participation of semi-volatile organic compounds in the later stage of the growth.

Unfortunately, there is no concurrent hygroscopicity data available during the study period presented in **Paper IV**. The evolution of hygroscopic growth factors at a constant relative humidity from a HTDMA gives an independent estimation on the mass fluxes of water soluble and insoluble components (Kulmala et al., 2001b), when converted to soluble volume fractions (Swietlicki et al., 1999). This was utilized in (**Paper III**), when variability in 10 and 20 nm particle hygroscopicity was analyzed during new particle formation event days. Growth of the newly formed particles were dominated by water soluble components under polluted conditions in Athens, Greece. When there was less anthropogenic influence, both of the components were participating the growth but mass flux of the water insoluble material was more pronounced. Tentatively this indicates that in a more polluted conditions, contribution soluble components

(e.g. sulphuric acid or soluble organics) is higher. This is corroborated by modeling (Stolzenburg et al., 2005a) and measurements (Smith et al., 2005; Sakurai et al., 2005) in sulphur rich and polluted Atlanta.

In a rural and sparsely populated areas e.g. Hyytiälä, Finland, where urban influence is by default less, same magnitude of variability in the calculated soluble and insoluble mass fluxes were detected already by Kulmala et al. (2001b) and confirmed by Ehn et al. (2006a) but it was not directly interlinked with anthropogenic pollution. To determine the effect of anthropogenic influence on growth of newly formed particles, three nucleation event days with a different exposure to anthropogenic pollution during its transport to a measurement site in Hyytiälä, Finland, were selected in **Paper VI**. All the selected cases were Arctic air masses, but on their way to Hyytiälä, one passed over Kola peninsula industrial area, one traveled over the city of Saint Petersburg in Russia and Narva area in Estonia, and a clean arctic reference case, which were not in contact with any major urban areas or industrial zones. The main finding was that hygroscopicity of nucleation mode particles varied only moderately, despite differences in the air mass transport routes. The particles were formed in the vicinity of a static measurement site and thus reflected more localized properties of precursors and condensable vapours. The larger particles, however, were transported a longer way. During their transport, they were subjected to composition changes due to sulphuric acid condensation (aging). This was detected as an increased hygroscopicity of 50 nm particles. This was in particularly imminent during a case, when the air mass had traversed through the Kola peninsula area, which is the largest source of sulphur compounds in the Arctic area (Kashulina and Reimann, 2001). When the exposure time to the pollution was shorter, hygroscopicity was lower as there was not enough time to sulphur dioxide to convert to sulphuric acid and to condense onto the transported particles.

Prior to **Paper V**, there was only a little experimental evidence of sulphuric acid condensation and subsequent increase in hygroscopicity (aging), in particularly in the ultra-fine size range. For the 50 nm particles the hygroscopicity is the key property determining, whether the particles can activate as a cloud condensation nuclei and thus contribute to the climate change indirectly.

## 4 Review of papers

The papers included into this thesis deal with field measurements of aerosol particles, data evaluation, and verification of the instrumentation in well defined laboratory conditions.

**Paper I** summarises and collects the existing information on observations of new particle formation and their subsequent growth under atmospheric conditions around the world. Gas-to-particle conversion seems to occur both in pristine areas as well as in anthropogenic pollution plumes.

**Paper II** presents data from a wide variety of field campaigns and continuous measurements, where new particle formation and growth was detected. Utilizing a relatively simple analytic framework, growth of the newly formed particles was transferred to concentration of vapours responsible for the observed growth. Also the source rate of these vapours was estimated assuming steady-state conditions. The growth and formation rates varied 2 orders of magnitude from 0.3 to 20 nm h<sup>-1</sup> and 1·10<sup>-4</sup>-7·10<sup>-2</sup> s<sup>-1</sup>, respectively. The source rate of condensable vapours, however, varied up to 4 orders of magnitude between the cleanest (Värriö in Finnish Lapland and Antarctica) and the most polluted (New Delhi) areas.

**Paper III** presents average atmospheric sub-micron aerosol size distribution as well as hygroscopic properties of selected nucleation and Aitken mode particle sizes based on two field campaigns in the surroundings of Marseille and Athens. New particle formation and subsequent growth was observed at both sites. Based on a diurnal cycle of hygroscopicity of 10 and 20 nm particles, the nucleation mode growth in Athens was dominated by water soluble components during polluted conditions and by water insoluble material, when clean air from the surrounding countryside advected to the measurement site.

**Paper IV** evaluates different growth processes relevant to nucleation mode particles and their relative magnitude at Melpitz, Germany. A volatility analysis of the newly formed particles revealed that 20-40% of the size increase was explained by accumulation of non-volatile core material. Remaining growth was mostly due to sulphuric acid condensation and to a smaller extent due to intra- and extramodal coagulation.

**Paper V** examines differences in hygroscopicity of Aitken (50 nm) and nucleation mode particles (10 nm and 20 nm) in Arctic Air masses based on three case studies.



The cases were selected based on air mass transport routes and their exposure time to anthropogenic sulphur pollution. The water vapour affinity of 50 nm particles was considerably higher, when the air mass traversed over industrialized Kola peninsula. Increase in hygroscopicity (aging) was due to condensation of sulphuric acid onto the particles traveling within the pollution plume. Newly formed particles, on the other hand, had similar hygroscopic properties regardless of the air mass origin. These particles were produced on the way to a measurement site in a boreal environment, and tentatively their chemical character was similar.

**Paper VI** verifies the performance of a recently developed Water Condensation Particle Counter TSI model 3785 (WCPC). A counting ability of the instrument varied as a function of super-saturation inside the apparatus. This enables fine-tuning of the WCPC to a desired cut-off diameter i.e. size, when 50% of the particles are successfully accounted for. Thus, it is possible to select a size of the sub-micron particles, larger which are counted successfully by the counter. The composition and solubility of the sampled particles had an effect on the detection efficiency. This is a drawback in a case of a single counter monitoring the number concentration of ambient particles of variable composition. But the WCPC is applied in parallel with an another counter relying on e.g. butanol condensation, new insights into the composition of atmospheric aerosol particles even below 10 nm in diameter could be extracted (Kulmala et al., 2006b)

## 5 Author's contributions

I'm solely responsible for the summary part of this thesis. In **Paper I**, I contributed to data collection from literature as well as participated in the collation of the formation and growth rates from a variety of sources into consolidated tables. In addition, I contributed in the writing on the measurement techniques. In **Paper II**, I was responsible for the production of the figures, wrote the instrumental setup and contributed to the conclusions as well as participated in the actual measurement campaign in Athens and Marseille. I was responsible for the hygroscopicity measurements presented in the **Paper III**, I wrote the article and did the data interpretation. In **Paper IV** I estimated the growth rate of newly formed particles due to coagulation with the pre-existing particle mode as well as due self-coagulation. I contributed to the interpretation of the results and participated in the writing process of the article as a whole. The idea

for the **Paper V** came up with discussions with W. Junkermann during a field campaign in Hyytiälä. For this paper, I conducted the hygroscopicity measurements and all the data-analysis except the OTDMA. I wrote the text except the sections related to the Organic TDMA. In the **Paper VI** I conducted sodium chloride measurements, analysed the data and wrote most of the text.

## 6 Conclusions

This thesis presents a global overview of new particle formation and subsequent growth of these particles as well as their spatial and temporal variability in the atmosphere. Gas-to-particle conversion is occurring worldwide. The spatial scale of formation ranges from regional to intensive local bursts, which typically produced  $1 \cdot 10^{-2}$ -10 and  $10^4$ - $10^5$  particles  $\text{cm}^{-3}\text{s}^{-1}$ , respectively. The exact formation mechanism remains unclear, and probably varies from location to location.

Growth rates of the freshly formed particles varies from fractions of nanometers per hour up to  $20 \text{ nm h}^{-1}$ . The highest growth rates were observed in polluted environments. Probably this is due to the strong interdependency between coagulation and condensational growth. Low particle growth is impossible with a high pre-existing particle population due to the effective scavenging (extramodal coagulation) of formed particles.

In this thesis, analytical methods were applied to determine a concentration of a condensable vapour and its' source rate, which would be able to explain the observed growth rates in environments from pristine Arctic and Antarctic regions to extremely polluted Indian urban atmosphere. The observed growth rates and calculated concentrations for the condensable vapours varied only 2 orders of magnitude, but the source rates for the vapours varied up to 4 orders of magnitude.

Indirect methods were applied to extract information about compounds resulting in the observed growth of the nucleation mode particles in the atmosphere. Volatility analysis and hygroscopicity measurements gave new insight on the compounds participating in the growth in Melpitz and Athens, respectively. In addition, laboratory verification of a newly developed Water Condensation Particle Counter revealed that it can be used to extract information on the composition of freshly formed particles in atmospheric conditions, when used in parallel with butanol based particle counters.

The newly formed particles grow by condensation of sulphuric acid, organic compounds and intramodal as well as extramodal coagulation in Melpitz, Germany. Non-volatile material explained 20-40% and sulphuric acid the most of the remaining growth up to a point, when nucleation mode reached 20 nm in diameter. Coagulation, explaining less than 5%, was only of a minor importance in Melpitz. Based on hygroscopicity changes in Athens, water soluble material (e.g. sulphuric acid) contributed more to the observed growth, when formation and subsequent growth occurred in an polluted air mass.

Whether or not the particles formed in the atmosphere can be of climatic importance depends crucially on their hygroscopic properties. In this study, air mass origin and transport routes were observed to have a dramatic effect on the water uptake of particles. Anthropogenic pollution increased the hygroscopic properties days after the initial contact with the sources. This influences also the ability of the particles to act as cloud condensation nuclei. Thus, it has a potential to even change precipitation patterns and cloud albedo downwind of the pollution sources.

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